Elucidation of Conditions for Metastable Poly(vinyl alcohol) Thin Films on Polydimethylsiloxane Substrates

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Introduction

Polydimethylsiloxane (PDMS)

- PDMS is a widely used polymer in the siloxane family. Its applications range from commercial products to cutting-edge scientific research because of its unique structure and properties.

- Compared to carbon-based polymers, PDMS has longer Si-O and Si-C bonds, larger Si-O-Si bond angle, and bonds with ionic character, giving rise to:

- High conformational flexibility
- High thermal stability
- Low glass transition temperature (~123 °C)
- High oxygen and water-vapor permeability
- Hydrophobicity

Poly(vinyl alcohol) (PVOH)

- Poly(vinyl alcohol) is a water-soluble and biodegradable polymer. It is atactic yet semi-crystalline on account of the hydroxyl group.

- PVOH is prepared via hydrolysis of poly(vinyl acetate)

- Degree of hydrolysis of PVOH = percent of acetate groups hydrolyzed to alcohol groups

A polymer thin film may manifest as a continuous film (stable, curve 1) or show dewetting patterns (unstable, curve 2), or both (metastable, curve 3). The effective interface potential ($\phi(h)$) has been studied with varying film thicknesses.

Three dewetting mechanisms, spinodal, thermal nucleation, and heterogeneous nucleation, can take place depending on the sign of $\phi''(h)$. Previous studies in our laboratory also discovered unusual dewetting morphologies, such as fractal features.

PVOH
PDMS
SiO _x
Si

Variables explored in this experiment include:

- PDMS molecular weight
- PVOH degree of hydrolysis
- PVOH solution concentration
- Spin rate

Objective

Through a comprehensive study on all the variables above, conditions were investigated to elucidate stable, metastable, and unstable regimes in the system. Focus was placed on low molecular weight PDMS substrates where PVOH thin films with metastability were observed.

Materials and Methods

Clean wafer preparation

- Cut into 1.4 x 1.4 cm² squares
- Rinse with distilled water and dry
- Clean with oxygen plasma

PVOH solution preparation

- PVOH^{99%_H}, MW = 89-98 kDa
- PVOH^{88%_H}, MW = 85-124 kDa
- PVOH solutions were heated at ~90 °C for 3 h
- Equilibrate for 3-4 days

PDMS substrates preparation

- PDMS MW = 237, 340, 770, 2k, 49k Da
- Drop cast 100 μ L of PDMS liquid onto silicon wafer
- Heat at 100 °C for 24 h
- Rinse with toluene, acetone and Milli-Q water
- Desiccate overnight

Fabrication of PVOH thin films via spin-coating

- Drop cast 400 μ L of PVOH solution onto each PDMS substrate
- Adsorb in air for 1 min
- Spin under N₂ for 1 min

Adsorption of PVOH (control)

- Pipette 400 μ L of PVOH solution onto each PDMS substrate
- Adsorb in air for 1 min
- Rinse by adding 2 mL of Milli-Q water
- Spin at 6000 rpm for 1 min to dry

Characterization

- Ellipsometry – thickness
- Goniometry – advancing and receding water contact angles
- Atomic force microscopy – surface topography

Conclusions

- Silicon wafer substrates containing low MW PDMS polymers are more hydrophilic than pure PDMS, which can be attributed to exposed silanol groups.
- Metastability of PVOH thin films was observed on low to intermediate MW PDMS substrates, PDMS²³⁷, PDMS³⁴⁰, PDMS⁷⁷⁰, and PDMS^{2k}.
- PVOH film thickness typically exhibits an exponential decay as a function of spin rate. On PDMS³⁴⁰ (low MW PDMS), the exponent increases as [PVOH^{99%_H}] increases, while the trend is the opposite for PVOH^{88%_H} films.
- 1 min static adsorption (control) experiments showed that variable amounts of PVOH adsorb as a function of PVOH degree of hydrolysis and concentration prior to spin, which could give rise to the opposite trends observed on PDMS³⁴⁰.
- The critical thickness for PVOH^{99%_H} is ~3 nm and that for PVOH^{88%_H} is ~5 nm, below which fractal and spinodal dewetting morphologies were obtained, respectively.

Future Plans

- Focus on thin film stability around the critical thickness on the metastable curves
- Distinguish between kinetic and thermodynamic stabilities of thin films prepared by spin coating

References

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Results

Effect of PDMS molecular weight on PVOH thin film morphology

AFM Images of PDMS substrates and PVOH^{99%_H} thin films fabricated on PDMS substrates (size: 1.25 μ m x 5 μ m; data scale: 5 nm)

Effect of spin rate on PVOH^{99%_H} thin films on PDMS³⁴⁰

Effect of spin rate on PVOH^{88%_H} thin films on PDMS³⁴⁰

Control experiments: static adsorption of PVOH^{99%_H} on PDMS³⁴⁰

- Substrates with intermediate and high MW PDMS polymers are hydrophobic.
- Lower contact angles on substrates with low MW PDMS polymers, e.g. PDMS³⁴⁰, are caused by thin PDMS layers and exposed silanol groups from underlying silicon wafer.
- Correlation between PVOH thickness and spin rate depends on PDMS MW, with exponents ranging from 0 (high MW) to -1 (low MW), indicating varying extents of thin film stability.
- On substrates containing PDMS with low to intermediate MWs, PVOH^{99%_H} films obtained at low spin rates are continuous while those obtained at high spin rates exhibit different dewetting morphologies. PVOH^{99%_H} thin films on these PDMS substrates are metastable.

- Adsorbed amount after 1 min increases as [PVOH] increases in a diminishing manner

- PVOH^{88%_H} adsorbs much more significantly than PVOH^{99%_H} on PDMS³⁴⁰

AFM Images of PVOH^{99%_H} thin films spin coated on PDMS³⁴⁰ as a function of spin rate and PVOH concentration (size: 1.25 μ m x 5 μ m; data scale: 5 nm)

- The exponent of thickness vs. spin rate curve increases as [PVOH^{99%_H}] increases.
- The critical thickness (from wetting to dewetting) of PVOH^{99%_H} thin films was found to be around 3 nm.
- Fractal morphologies were observed on dewetted PVOH^{99%_H} thin films.

AFM Images of PVOH^{88%_H} thin films fabricated on PDMS³⁴⁰ as a function of spin rate and PVOH concentration (size: 1.25 μ m x 5 μ m; data scale: 5 nm)

- The exponent of thickness vs. spin rate curve decreases as [PVOH^{88%_H}] increases.
- The critical thickness of PVOH^{88%_H} thin films was found to be around 5 nm.
- Spinodal dewetting was observed on 0.2 wt.% PVOH thin film obtained at 6000 rpm.